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13. ABSTRACT (Maximum 200 words) Our research into the chemical properties of highly vibrationally excited molecules has revealed a strong connection between large amplitude vibrational motion and the ability of a molecule to accept or donate electrons. In this proposal, we explain the work leading up to this insight and suggest ways to further test our understanding of this phenomenon. We suggest two experiments to extrapolate these results to completely new kinds of chemical encounters: the vibrational enhancement of electron capture and the direct observation of vibrational promotion of an electron transfer reaction. This work may have significant implications for electron scavenging around re-entry vehicles and accompanying communications blackouts. 20011126 116		
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Final Technical Report

Reactive" vibrational relaxation in the Gas-Phase and on Surfaces", : F49620-98-1-0173, March 1, 1998-Feb.328 2001

Approach

Understanding the gas-phase and gas-surface collision dynamics of highly vibrationally excited NO is necessary to model the chemical reactivity, ro-vibrational population distribution and infrared emission spectrum of this important molecule in the upper atmosphere. There is increasing evidence that collisional relaxation of highly vibrationally excited molecules may be controlled by very unusual state-to-state cross-section associated with new dynamics that are not found for the low vibrational states.

The objective of this research is to understand and characterize new mechanisms as well as to predict and control the chemical reactivity and the flow of energy in such highly vibrationally excited molecules. Topics of interest include: the effect of vibrational excitation on reaction probability, chemical branching and survival probability of vibrationally excited NO upon collision with other molecules and surfaces. Experimental results can then be used in atmospheric chemistry and space vehicle emission modeling.

Quantum state selective laser-based optical pumping schemes such as stimulated emission pumping (SEP) and overtone pumping are used to prepare NO molecules in low and high vibrational states for comparison. Crossed molecular beams methods are used to study the rotational and vibrational energy transfer as well as chemical reactivity of these species under single collision conditions. Velocity mapping techniques are used to obtain product angular and velocity distributions. Ultra-high vacuum surface-science methods are combined with SEP and molecular beam techniques to study gas-surface interaction for the first time.

Results

We have developed and presented a new experimental method for measurement of collision-free infrared radiative lifetimes for single quantum states of a vibrationally excited sample. This method provides a more direct route to the infrared Einstein A-coefficients than has been previously possible. Results for NO($X^2\Pi$, $v=21$ and $v=7$) were presented. Comparison to results of *ab initio* calculations shows excellent agreement. A controversy regarding the relative intensities of 1st-overtone and fundamental emission intensities in NO is laid to rest. The most complete least squares analysis of existing data was carried out to derive the electric dipole moment function (EDMF) to an accuracy of $\pm 0.02D$ between 0.9 and 1.7 Å.

In another study we have investigated near resonant vibration-vibration energy transfer. Lack of understanding of the factors that compensate energy defects in near resonant V-V energy transfer constrains our ability to accurately predict resonance widths and, thus, the overall importance of such processes. We have carried out one of the first truly state-to-state measurements of near resonant V-V energy transfer under single collision conditions, employing the crossed molecular beams, stimulated emission pumping technique. We have varied the energy defect ΔE for the process: NO $X^2\Pi(v=1)+N_2O(0,0,1)$, by changing the prepared vibrational state from $v=22$ ($\Delta E = +14 \text{ cm}^{-1}$) to $v=21$ ($\Delta E = -18 \text{ cm}^{-1}$) to $v=20$ ($\Delta E = -49 \text{ cm}^{-1}$). Changes in the energy transfer efficiencies and rotational distributions of vibrationally inelastically scattered NO with energy defect both strongly suggest that molecular rotation (both of NO and N_2O) is responsible for compensating the energy defect. Furthermore it appears that relative translation is ineffective in compensating the energy defect.

Much of our work over the funding period has been geared toward trying to understand molecular interactions with metal and oxide surfaces. We developed and presented a new experimental approach to the study of vibrational relaxation of highly vibrationally excited molecules at solid surfaces. We observed NO in $v=13$ and 15 losing up to five vibrational quanta in collisions with an O-covered copper surface. The data indicated this vibrational relaxation occurs via a direct scattering mechanism.

These studies were then expanded to study vibrationally promoted surface chemistry. The chemical dynamics of highly vibrationally excited molecules were studied by measuring the quantum state-resolved scattering probabilities of nitric oxide (NO) molecules on clean and oxygen-covered copper (111) surfaces, where the incident NO was prepared in single quantum states with vibrational energies of as much as 300 kilojoules per mole. The dependence of vibrationally elastic and inelastic scattering on oxygen coverage strongly suggests that highly excited NO ($v = 13$ and 15) reacts on clean copper (111) with a probability of 0.87 ± 0.05 , more than three orders of magnitude greater than the reaction probability of ground-state NO. Vibrational promotion of surface chemistry on metals (up to near-unit reaction probability) is possible despite the expected efficient relaxation of vibrational energy at metal surfaces.

In light of all of the new results on very highly vibrationally excited molecules, we decided to perform some experiments on lower vibrational states as well. Measurements of vibrational excitation and de-excitation of NO ($v = 2$) scattering from a Au(111) surface show that the probability of both processes increases strongly with the kinetic energy of the incident NO. These results were qualitatively consistent with a vibrational energy transfer mechanism involving electron-hole pairs but not with competing adiabatic models. The form of the energy dependence, and other features of the measurements, are not in accord with existing calculations.

One of our most exciting results used laser methods to prepare specific quantum states of gas-phase nitric oxide molecules, where we examined the role of vibrational motion in electron transfer to a molecule from a metal surface free from the complicating influence of solvation effects. The signature of the electron transfer process was a highly efficient multi-quantum vibrational relaxation event, where the nitrogen oxide loses hundreds of kilojoules per mole of energy on a sub-picosecond time scale. These results cannot be explained simply on the basis of Franck-Condon factors. The large-amplitude vibrational motion associated with molecules in high vibrational states strongly modulates the energetic driving force of the electron transfer reaction. These results show the importance of molecular vibration in promoting electron transfer reactions, a class of

chemistry important to molecular electronics devices, solar energy conversion, and many biological processes.

Publications resulting from AFOSR support

1. *Infrared and collisional relaxation of highly vibrationally excited NO: Applications of stimulated emission pumping in crossed and Auncrossed \cong molecular beams*, Marcel Drabbels and Alec M. Wodtke, in Highly Excited Molecules: Relaxation, Reaction and Structure, Eds. A.S. Mullin, G.C. Schatz, ACS Symposium Series, v. 678, p. 173 (1998)
2. *Rotational motion compensates the energy defect in near-resonant vibration-vibration energy transfer*, M. Drabbels, A.M. Wodtke, J. Chem. Phys. **109**, 355-258 (1998)
3. *Determination of rotational polarization using 1+1' REMPI: A case study of D₂ associative desorption from Cu(111)*, H. Hou, S.J. Gulding, C.T. Rettner, A.M. Wodtke, D.J. Auerbach, J. Electron Spectrosc., **98-99**, 133-138 (1999);
4. *Direct multi-quantum relaxation of highly vibrationally excited NO in collisions with an O-covered Copper surface*, H. Hou, Y. Huang, C.T. Rettner, S.J. Gulding, D.J. Auerbach, A.M. Wodtke, J. Chem. Phys. **110**, 10660-10663 (1999).
5. *Enhanced Reactivity of Highly Vibrationally Excited Molecules on Metal Surfaces*, H. Hou, Y. Huang, S.J. Gulding, C.T. Rettner, D.J. Auerbach A.M. Wodtke, Science **284**, 1647-1650 (1999)

6. *Collisions and chemistry of super-excited molecules: experiments using the PUMP - DUMP - PROBE technique*, Marcel Drabbels and Alec M. Wodtke, Feature Article for J. Phys. Chem. , **103** 7142-7154 (1999)
7. *The Interaction of Highly Vibrationally Excited Molecules with Surfaces: Vibrational Relaxation and Reaction of NO(v) at Cu(111) and O/Cu(111)*, H. Hou, C. T. Rettner, D. J. Auerbach, Y. Huang, S.J. Gulding, A.M. Wodtke, Faraday Discuss. **113**, 181-199 (1999)
8. *Observation of vibrational excitation and de-excitation for NO(v=2) scattering from Au(111): Evidence for electron-hole pair mediated energy transfer*, Y. Huang, A.M. Wodtke C.T. Rettner, and D.J. Auerbach, Phys. Rev. Lett. **84** 2985-8 (2000)
9. *Vibrational Promotion of electron transfer*, Y. Huang, S.J. Gulding, C.T. Rettner, D.J. Auerbach A.M. Wodtke, Science **290**, 111-114 (2000)
10. *Rotational Analysis of the origin and the inversion bands in the $S_1 \leftarrow S_0$ spectrum of acetaldehyde*, E. Jalviste, G. Berden, M. Drabbels, A. M. Wodtke, J. Chem. Phys. **114**(19) 8316-27 (2001)
11. *Dipole moments of highly vibrationally excited HCN: theoretical prediction of an experimental diagnostic for delocalized states*. Joel M. Bowman, Stephen Irle, Keiji Morokuma, Alec Wodtke, Journal of Chemical Physics **114**(18) 7923-34 (2001)

12. *The Dynamics of "Stretched Molecules": Experimental Studies of Highly Vibrationally Excited Molecules With Stimulated Emission Pumping*, Michelle Silva, Rienk Jongma, Robert W. Field Alec M. Wodtke, Annual Reviews of Physical Chemistry **52**, 811-852 (2001)
13. *Chemistry with stretched molecules*, Alec Wodtke, Phys. Chem. Earth (C) **26**(7), 467-471 (2001)
14. Mathematica notebook to calculate Wigner 9-J Symbols, A.M. Wodtke, Joushua Halpern, <http://www.mathsource.com/cgi-bin/msitem?0210-890>, December, 1999

Public scientific presentations of AFOSR supported work

1. AFOSR contractors Meeting, Monterrey California, May17-20, 1998, "Crossed-beam and surface scattering of highly vibrationally excited NO"
2. Seminar at the Department of Physics at University of Leiden, Holland, June 17 1998, "Alignment of recombinatively desorbed hydrogen from Cu(111): quantum state and velocity dependence"
3. Poster Presentation "Chemical Interactions of Super excited molecule on Metal surfaces" Gordon Research Conference of Chemical Reactions at Surfaces, Ventura California ,Feb. 28-March 4 1999

4. Invited Lecture, "Chemical Interactions of Super excited molecule on Metal surfaces", Department of Chemistry, Swiss Federal Institute of Technology Lausanne.
June 16 1999
5. Invited Lecture, "Collisions and Chemistry of Super Excited molecules" Conference of Molecular Energy Transfer, COMET XVI, Assisi, Italy, June 20-25 1999
6. Poster Presentation, "Chemical Interactions of Super-Excited Molecules on Metal Surfaces", H. Hou, C.T. Rettner, D.J. Auerbach, Y. Huang, S.J. Gulding, A.M. Wodtke, Conference of Molecular Energy Transfer, COMET XVI, Assisi, Italy, June 20-25 1999
7. Invited Lecture, "Controlling Reagent Vibration: A Key To Understanding Chemical Dynamics At Surfaces", Gordon Conference On Dynamics At Surfaces, Andover NH, August 8-13, 1999
8. Invited Lecture, ACS Regional Meeting, Oct. 6-7, 1999.
9. Invited Lecture, "Chemistry with stretched molecules", Department of Chemistry Colloquium Series, University of Arizona, Oct. 14, 1999.
10. Invited Lecture, "Chemical interactions of Super-Excited Molecules on Metal Surfaces", University of Utah, P-Chem. Seminar, Oct. 18, 1999.

11. Community Outreach, "19 2nd graders from La Patera School tour the lab", Jan. 14 2000
12. Invited Lecture, "Chemistry with stretched molecules", Department of Chemistry Colloquium Series, Emory University, Feb. 10, 2000.
13. Invited Lecture, "Chemistry with stretched molecules", Department of Chemistry Chemical Physics Seminar Series, California Institute of Technology, April 4, 2000.
14. Invited Lecture, "Chemistry with stretched molecules", FOM for Plasma Physics Rijnhuizen, The Netherlands, April 26, 2000
15. Invited Lecture, "Chemistry with stretched molecules", European Geophysical Society Meeting, Nice France, April 28, 2000.
16. Invited Lecture, "Chemistry with stretched molecules", Department of Chemistry EPFL, Lausanne Switzerland, May 1 2000.
17. Invited Lecture, "Chemistry with stretched molecules", Department of Physics University of Bielefeld Bielefeld, Germany May 3, 2000.

18. Invited Lecture, "Chemistry with stretched molecules", AFOSR Contractors Meeting, Waltham, MA, May 22, 2000.
19. Invited Lecture, "Chemistry with stretched molecules", Institute of Atomic and Molecular Science (IAMS), Taipei Taiwan, June 12, 2000
20. Invited Lecture, "Chemistry with stretched molecules", Synchrotron Radiation Research Center, Hsinchu, Taiwan, June 13, 2000
21. Invited Lecture, "Chemistry with stretched molecules", CECAM Workshop on Molecular Aspects of Gas Dynamics, Lyon France, June 28
22. Invited Lecture, "Chemistry with stretched molecules", University of Kiel, Physical Chemistry Colloquium, Kiel Germany, June 29 2000.
23. Invited Lecture, "Chemistry with stretched molecules: Vibrational promotion of an electron transfer reaction", Pacificchem 2000, Symposium on "Photon and Electron Induced Processes on Surfaces", December 14 - 19, 2000, Honolulu, Hawaii
24. Poster Presentation: Gordon Research Conference on Molecular Energy Transfer, "Combining Stimulated Emission Pumping with Hexapoles", 1/14/2001-1/19/2001, Ventura California